# Performance and Characterization of Irradiated Poly (vinyl alcohol)/Polyvinylpyrrolidone Composite Hydrogels Used as Cartilages Replacement

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**ABSTRACT:** In this article, hydrogels were prepared by compounding Polyvinylpyrrolidone (PVP) with Poly (vinyl alcohol) (PVA), which is used as artificial cartilages, by means of repeating freezing and thawing and irradiation, for improving their mechanical and surface lubricative properties. The structures and properties, including gel content, crystallized degree, elastic modulus, and frictional coefficients of the compound hydrogels with different PVP contents and irradiative conditions, were examined and compared. The existence of PVP macromolecules interfered with the crystallization of PVA hydrogels resulted in the decrease of gel contents and elastic modulus, as well as the unstable external frictional coefficient in water. After irradiation treatment, these performances increased with irradiation intensity in lower dose ranges. The solubility and exudation of PVP in water were prevented and reduced because of the chemical crosslink of PVA and PVP, and the lubricative properties of PVA/PVP hydrogels in water were improved. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 736–741, 2009

**Key words:** biomaterials; hydrogels; irradiation; poly(vinyl alcohol); Polyvinylpyrrolidone

## INTRODUCTION

The use of polymer hydrogels to replace damaged tissues is a promising incentive for their good biocompatibility in contact with human tissues.[1–3] Crosslinked Poly(vinyl alcohol) (PVA) hydrogels with high water contents possess good biocompatibility, high elasticity and mechanical strength, and good chemical stability and durability, could have been used as promising artificial cartilage.[4–6] The general methods of clinical therapies for damaged cartilage are cartilage transplantation or prosthetic replacement.[7,8] The former is always limited by donor tissue availability and donor site morbidity, and the latter always use the metal, ultra-high molecular weight polyethylene, silicone rubber, and polyurethane soft pad and so on.[9–11]

According to the physiological functions of arthrosis, articular cartilages serve as soft conjoin cushion between bone, which could transfer and distribute the laden stress equably, and reduce the friction and abrasion in human arthrosis.[12,13] Surface lubricative and biomechanical properties are important to articular cartilages to protect arthrosis. Nevertheless, the surface of PVA hydrogel, as well as other artificial materials, has bad interface lubricative property because of the strong action of hydrogen bond formed among molecules. These disadvantages limited the applications of PVA hydrogels as cartilage substitute. The compound hydrogels of PVA with other bioactive materials have been investigated. Kobayashi et al. researched collagen immobilized PVA hydrogel-hydroxyapatite used as peripheral cuff of artificial cornea.[14] The preparation and *in vitro* behaviors of PVA-hydroxyapatite hydrogel used as cartilage were also studied.[15,16] Lin et al. and Xiao and Yang researched the preparation and blood compatibility of poly(glutamic acid)/polyvinyl alcohol hydrogels,[17] starch-g-PVA hydrogel,[18] and PVA/EDTA hydrogels.[19]

Polyvinylpyrrolidone (PVP), one kind of water soluble polymers, with excellent biocompatibility and surface activity has been used as a lubricant, also as main component of temporary skin covers or wound dressings.[20,21] To improve the surface and friction properties of artificial cartilage, composite hydrogels were prepared by compounding PVP with PVA. The wear and friction characteristics of PVA/PVP hydrogels and three correlative factors, including polymer content, load, and effect of lubricant, were studied by Katta et al.[22] The performance

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and biocompliant properties of PVA/PVP hydrogels cartilage with two different moduli were explored by implantation into osteochondral defects in a rabbit model *in vivo*.[23]

However, in PVA/PVP hydrogels, the rigid chain of PVP macromolecules interfered with the crystallization of PVA molecules and the gel formation, which result in the decrease of mechanical properties. Furthermore, PVP molecules in the compound hydrogels without chemical crosslink tend to dissolve gradually in water in physiological environment, led to the deterioration of their performance.[24] Therefore, the irradiation crosslink steps were introduced to the process of PVA/PVP hydrogel formation. Chemical crosslink would be formed between PVA and PVP molecules through the reaction of both macromolecular free radicals produced during irradiation.[25] This process could increase the crystallization and gel formation of hydrogels, and also influence the mechanical and surface properties consequently.[19] In this work, PVA/PVP hydrogels were prepared by method of repeating freezing and thawing, and following were treated with irradiation. The gel content and crystallized degree of compound hydrogels with different PVP contents and irradiative conditions were measured. The mechanical and lubricated properties of hydrogels were examined and compared before and after irradiation.

## EXPERIMENT

### Preparation of PVA/PVP compound hydrogels

PVP solution was made by dissolving proper rations of PVP (K30, from Beijing Yili Chemical Co.,China) in water and mixing around until PVP dissolved completely. PVA solutions (20 wt %) were prepared by dissolving proper rations of PVA (molecular average weight being about 79,000, the degree of alcoholysis of 99%, Guizhou chemical agent factory, China) in distilled water at 90°C with stirring for 3–5 h. The homogeneous PVA and PVP solutions were mixed round continuously under ultrasonic dispersive instrument at 85°C more than 4 h, and then, air bubbles in solution were removed. The concentration's ranges of PVP were 10–40 wt %. The compound hydrogel were obtained by casting the mixture in the mold and frozen at −20°C for 6–10 h, then thawed at room temperature for another 6–10 h. This freeze–thawing procedure was repeated four times. Then PVA/PVP hydrogels was exposed to 60 Co -rays at ambient temperature with different irradiative time and doses.

### Gel content and crystalline degree

Gel content of the PVA/PVP hydrogels was measured according Park and Nho[21] by extraction in distilled water at 80°C for 72 h and vacuum dried more than 48 h until they reached constant weight. The gel content was calculated as the following equation:

$$\text{Gel content} = W_2/W_1 \times 100\%,$$

Where $W_2$ is the dried gel weight after extracting, and $W_1$ is the initial weight of the PVP and PVA. Three parallel samples were measured at the same times, and the average gel contents were calculated.

Crystalline degrees were measured with differential scanning calorimetry (DSC), calefactive rate was 10°C/min, scanning temperature range was 50–250°C. The crystalline degree (Xc) was calculated as former work[26].

### Mechanical and lubricative properties

The mechanical properties of the PVA/PVP hydrogels were measured using LJ-500 Testing Instrument (China). Column samples in size of $\phi$ 15 mm × 30 mm were used for compressive test according to the criterion GB527-76 of China. The stress and strain curves were measured and compressive modulus were calculated. The frictional coefficients of PVA/PVP hydrogels were measured by UMT-2 micromechanical instrument (Center of Tribology,USA). Smooth PVA/PVP hydrogels with and without irradiation, in the size of 20 mm × 20 mm × 2 mm, placed on underside sample-board, the move rate of experimental plate was 2 mm/s, the load was 250*N*. The frictional coefficients was gained and calculated in 5 s from ten tests.

## RESULTS AND DISCUSSION

### The lubricative properties

Many factors have an important influence on the lubricative properties of PVA/PVP compound hydrogels, including water and PVP contents, molecular crosslink and action of hydrogen bond, and so on. The inner hydrogen bond and stable structure with hexahydric ring formed between polyvinyl alcohol molecules could lead to the limitation of lubrication action for PVA hydrogels.[24] The frictional coefficient of PVA/PVP hydrogels between hydrogels and testing plate were measured, and the relationships of frictional coefficient of hydrogel with different PVP contents before and after irradiation were showed in Figure 1. The lubricative properties of PVA/PVP were improved greatly compared with that of PVA. It could be seen that the friction coefficient declined continuously with the increase of PVP contents, because of the lubricative action of PVP molecule. After irradiation, the friction coefficient of

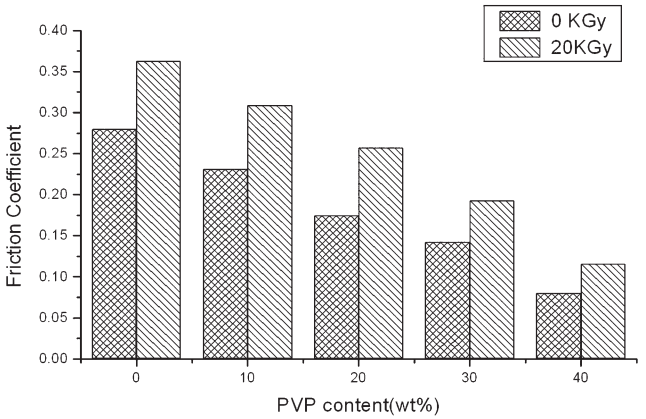
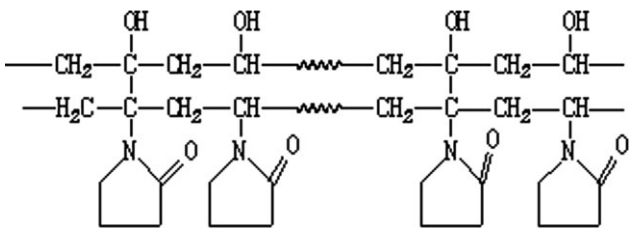



**Figure 1** Frictional coefficient versus PVP contents with and without irradiation treatment.

the hydrogels went up, which meant that the lubricative properties decreased. It was because that the irradiation result in the chemical crosslink between PVA and PVP, which might reduce the lubricative action of PVP molecule. The chemical crosslink structures formed between PVA and PVP molecules through the reactions of both macromolecular free radicals produced in irradiation process were showed as follow:



As artificial cartilage, PVA/PVP hydrogels were used in aquiferous and physiological condition, and it was necessary to increase their stability in water. Although the irradiation resulted in the decline of lubricative performance of PVA/PVP hydrogels, the stability of PVP in hydrogels in water would be improved. Figure 2 showed the friction coefficients of PVA/PVP hydrogels changed with time in water. Without irradiation treatment, the friction coefficients of PVA/PVP hydrogels increased rapidly after immersed in water because of the dissolution and exudation of PVP from hydrogels. The deliquescent process could induce the decline of the lubricative properties of hydrogels [Fig. 2(A)]. After irradiation, the friction coefficients of PVA/PVP hydrogels were more stable and had not changed almost until 18 days in water [Fig. 2(B)]. It was because that the dissolution and exudation of PVP was prevented or reduced due to the chemical crosslink between PVA and PVP. These PVA/PVP hydrogels with chemical crosslink in irradiation could not be dissolved completely in water at 95°C more than 2 h, while those

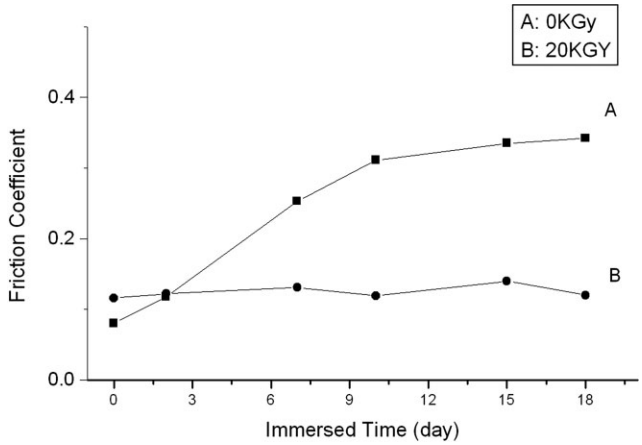



**Figure 2** Changes of friction coefficient of PVA/PVP hydrogels in water with and without irradiation treatment.

hydrogels by freezing and thawing dissolve within 1 h. This also indicated the chemical crosslink improving the stability of PVA/PVP hydrogels.

### Gel content and crystalline degree

The gelation of PVA/PVP hydrogels was formed by physical and chemical crosslinks, which was produced by the process of freeze–thawing and irradiation, respectively. Figure 3 showed the gel contents of PVA/PVP hydrogels with different PVP contents and irradiation dose. Without irradiation, gel contents of the hydrogels were in range of 23–57%, which decreased as PVP content increased. In freezing and thawing process, the gelation of hydrogels was caused by physical crosslink. The existing of PVP reduced the formation of gel only with physical crosslink (curve A in Fig. 3). After irradiation, the gel contents of PVA/PVP hydrogels were up to 85%, and increased a little with the increase of PVP contents (curve B in Fig. 3). The gelation of hydrogels prepared by irradiation was larger than that only by

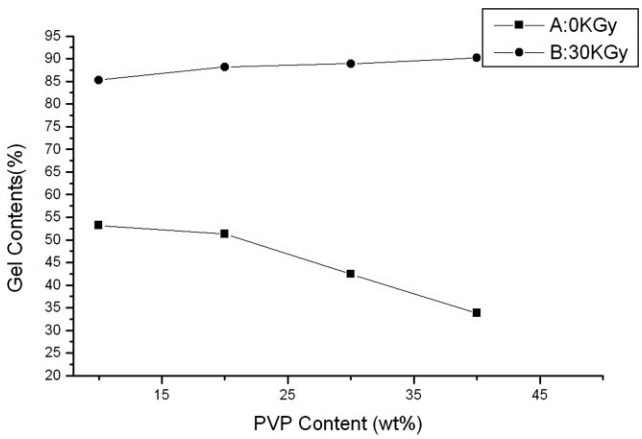



**Figure 3** Changes of gel contents with different PVP contents before and after irradiation.

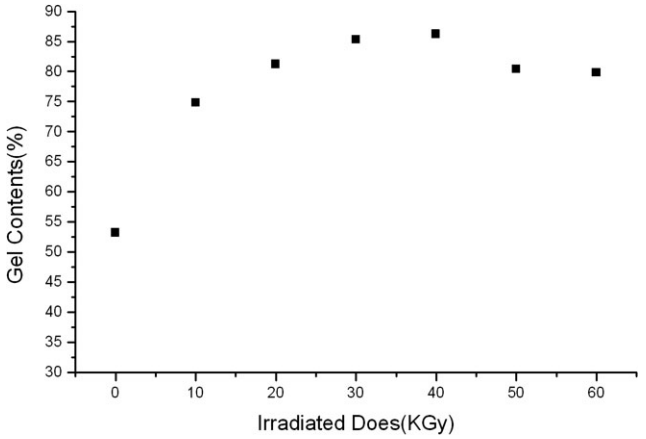



**Figure 4** Changes of gel contents with different irradiated doses.

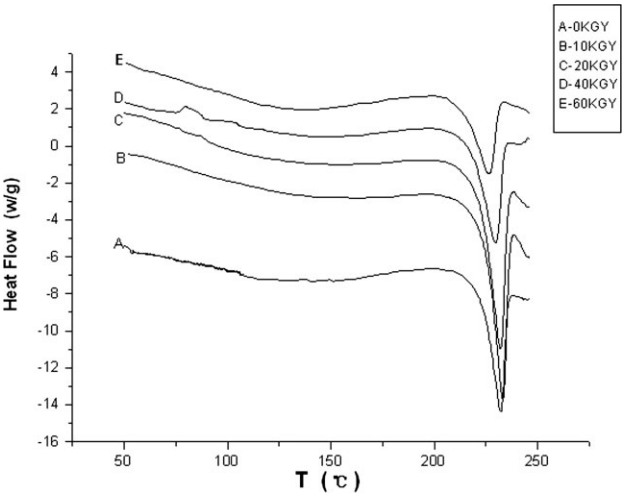



**Figure 6** DSC exothermic curves of PVA/PVP hydrogels treated with different irradiation dose.

freezing and thawing. However, the gel contents did not change proportionally with the increase of irradiation dose (Fig. 4). When the dose below 40 KGy, gel contents increased as irradiation dose increased. These results indicated that exist of PVP did not reduced the formation of gel of PVA/PVP hydrogels when treating with irradiation after freeze-thawing, and the increase of higher irradiation doses could improved gel contents of hydrogels.

For PVA, the formation of crystallites during the freeze–thawing serves as physical crosslinks. However, the rigid chain of PVP macromolecules interfered with the crystallization of PVA molecules in PVA/PVP hydrogels. Figure 5 showed the crystalline degree of hydrogels decreased as the increase of PVP contents. The crystalline degree of hydrogels was 58% without PVP, and the data was reduced to 41% with PVP contents of 30%. Figure 6 was exothermic curves of PVA/PVP hydrogels treated with different irradiation dose measured by DSC. The crystalline degrees of hydrogels were calculated from the exothermic peaks shown in Figure 7. It could be seen that crystallization of hydrogels decreased as the increase of irradiation dose and PVP contents. Nevertheless, the gel contents increased as increase of irradiation dose (see Fig. 4), which meant that the gelations in PVA/PVP hydrogels with irradiation were caused not only by physical crystallization, but also by the chemical crosslink of PVA and PVP. In other words, the chemical crosslinks also contributed to the formation of gels in PVA/PVP with irradiation treatment, which resulted in the different changes of crystalline degrees and gel contents as increase of irradiation dose and PVP contents.

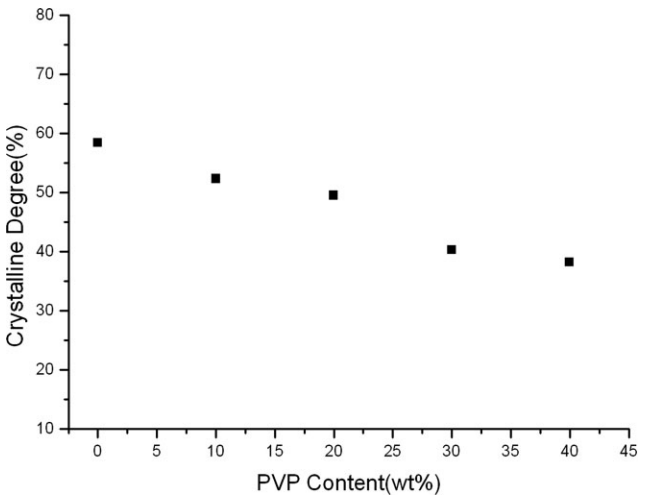



**Figure 5** Crystalline degree of compound hydrogels versus PVP contents.

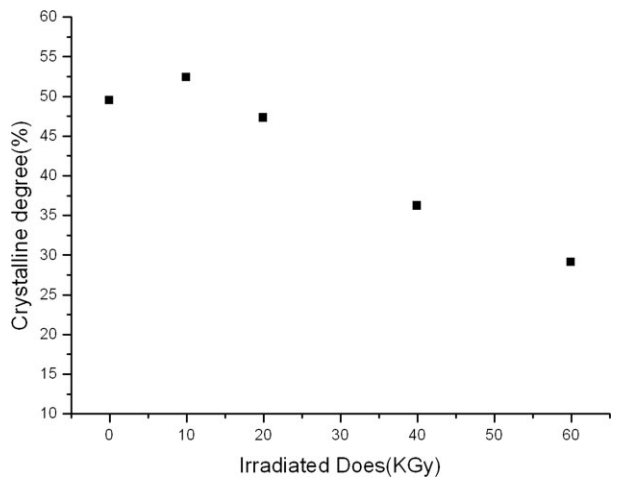



**Figure 7** Changes of crystalline degree of hydrogels with irradiated doses.

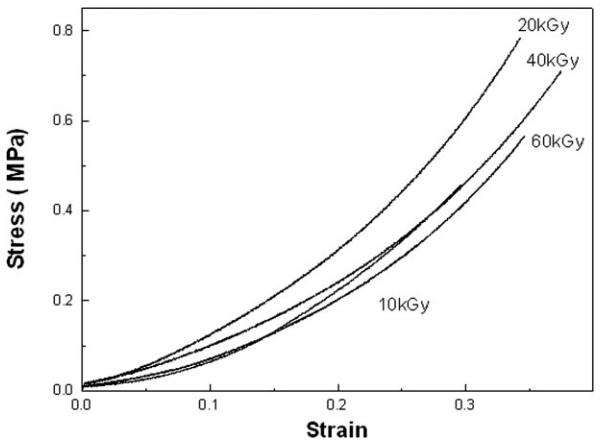



**Figure 8** Stress/strain curves for PVA/PVP hydrogels with different irradiation doses.

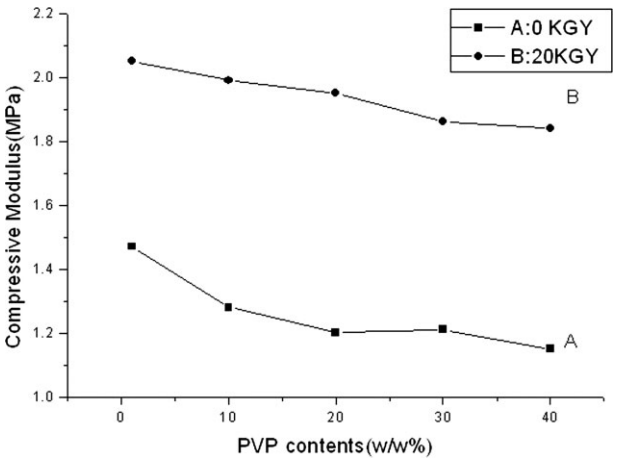



**Figure 10** Elastic modulus of PVA/PVP hydrogels with different PVP contents before and aftert irradiation.

## Mechanical properties

During irradiated process of PVA/PVP hydrogels, the chemical crosslink and degradation occurs simultaneously. The crosslink transforms a linear polymer into a three dimensional molecule, and results in a significant increase in molecular mass and mechanical properties, also reduces the solubility of the polymer in solvents or water. The degradation has the opposite effect. However, the ratio of crosslink depends on the chemical structure and physical state of the polymer, and the irradiation conditions. There are many factors which influence the mechanical properties of PVA/PVP hydrogels, including irradiation dose, PVP contents, gelation, and so on. Figures 8 and 9 showed compressed stress/strain curves and the elastic modulus of PVA/PVP hydrogels with different irradiative doses. The elastic modulus was 1.48 MPa when the hydrogels were made only by freeze–thawing method. After irradiation treatment, the elastic modulus increased to 1.83 MPa. It could be seen that the elastic modulus of hydrogels changed unproportionatly with the increase of irradiation dose. When the dose below 30 KGy, elastic modulus increased as irradiation dose increased. On the contrary, when over 40 KGy, those data decreased with the increase of irradiation dose. This phenomenon reflected the coaction of crosslink and degradation during irradiation. In high irradiation intensity, more degradation would occur resulting in the decline of the mechanical properties.

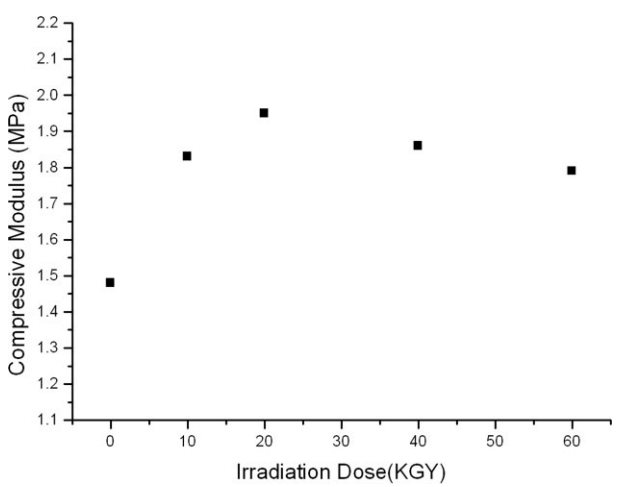



**Figure 9** The elastic modulus of PVA/PVP hydrogels with different irradiation doses.

Figure 10 showed the elastic modulus of PVA/PVP hydrogels changed with the PVP contents before and after irradiation treatment. It could be seen from curve A that the modulus decreased obviously with the increase of PVP contents for those hydrogels without irradiation, which indicated that the existence of PVP caused the mechanical properties of hydrogels declined. This was owing to the decrease of crystallization and gelation of PVA/PVP hydrogels caused by the macromolecular interferer of PVP without irradiation (see Figs. 3 and 4). Whereas, after irradiated treatment, the elastic modulus of PVA/PVP hydrogels did not decrease obviously as the increase of PVP contents (see Fig. 10 curve B), which meant the irradiation process improved the mechanical properties of PVA/PVP hydrogels. It was because that the chemical crosslink between PVA and PVP during irradiation process resulted in the increase of gel formation, and conduced consequently the increase of mechanical performance.

## CONCLUSIONS

PVA/PVP hydrogels prepared by method of repeating freezing and thawing, and following treated with irradiation could form the physical and chemical crosslink respectively, which result in the changes of the gel content, crystallization, and

mechanical properties of the hydrogels. The gel content of PVP-PVA compound hydrogels became larger than that only by freezing and thawing, but did not change obviously with the increase of PVP contents. While crystallization of compound hydrogels decreased as the increase of irradiation dose. The existence of PVP macromolecules interfered with the crystallization of PVA hydrogels, and resulted in the decrease of gel contents and elastic modulus. The friction coefficient of PVA/PVP hydrogels declined continuously with the increase of PVP contents. Without radiation treatment, the friction coefficient of PVA/PVP hydrogels increased rapidly in water. With radiation, the solubility and exudation of PVP from hydrogels could be prevented, and lubricative properties of PVA/PVP hydrogels in water were improved.

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